



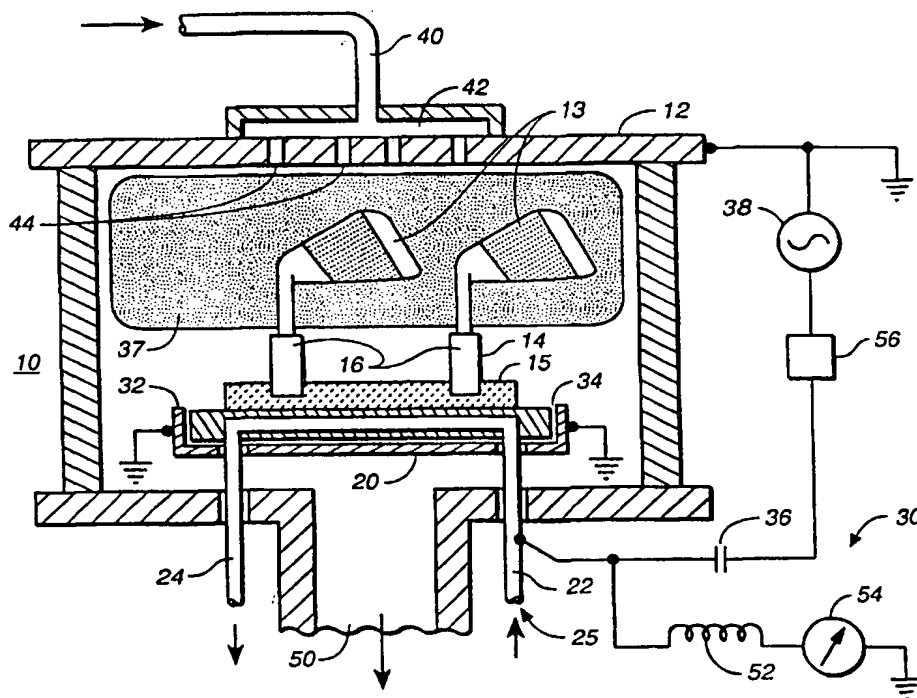
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(54) Title: HIGHLY DURABLE AND ABRASION RESISTANT COMPOSITE DIAMOND-LIKE CARBON DECORATIVE COATINGS WITH CONTROLLABLE COLOR FOR METAL SUBSTRATES

## (57) Abstract

The invention provides a highly durable and abrasion-resistant composite diamond-like carbon coating with controllable color which is ideally suitable as a decorative coating on electrically conductive substrates (13, 71). The composite diamond-like carbon coating structure consists of at least a first layer of Si-DLC which comprises the elements C, H, Si and possibly O and N. An additional coating containing layers of Si-DLC and DLC may be applied over top of the first Si-DLC layer. The decorative and abrasion-resistant composite diamond-like carbon coating is deposited by ion-assisted plasma deposition from carbon-containing and silicon-containing precursor gases consisting of hydrocarbon, silane, organosilane, organosilazane and organo-oxy silicon compounds, or mixtures thereof, and has the properties of Nanoindentation hardness in the range of approximately 5 to 35 GPa, modulus in the range of approximately 50 GPa to 300 GPa, and a thickness in the range of approximately 1 to 25 micrometers.



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# HIGHLY DURABLE AND ABRASION RESISTANT COMPOSITE DIAMOND-LIKE CARBON DECORATIVE COATINGS WITH CONTROLLABLE COLOR FOR METAL SUBSTRATES

This application is based on provisional application Serial No. 60/074,297, filed on February 11, 1998.

## FIELD OF THE INVENTION

This invention relates generally to highly durable and abrasion-resistant decorative coatings. More particularly, the invention relates to a process for depositing a highly durable and abrasion-resistant composite diamond-like carbon coating with controllable color. The invention is particularly suited for applications as a highly durable decorative coating on electrically conducting substrates which are subjected to high wear environments including architectural hardware and fixtures made of brass and other metals, jewelry, medical and dental instruments, writing instruments such as pens and pencils, musical instruments, eyeglass frames, cigar and cigarette lighters, automobile hood ornaments and other components, sporting equipment and other products for leisure activities such as golf club shafts, golf club heads, cycling equipment, and fishing and hunting equipment, and other similar substrates.

## BACKGROUND OF THE INVENTION

There have been many attempts to provide cosmetically attractive protective coatings onto sporting equipment such as golf club shafts, golf club heads, cycling equipment, fishing and hunting equipment, and other hardware. A wide variety of metal substrate materials are used in these applications, including steels, stainless steels, aluminum, zinc, brass, titanium, and specialty alloys such as aluminum alloys, titanium alloys, magnesium alloys, zinc alloys, and copper alloys. Coatings can improve the cosmetic appearance of these substrate materials, since many naturally have a dull finish or drab color. In addition, most of these substrate materials quickly develop a dull appearance due surface oxidation or corrosion resulting from exposure to environmental conditions such as high temperature, humidity, salt, and acid rain. Therefore, decorative protective coatings are often applied to these substrates to improve their cosmetic appearance, and environmental durability.

Typically, the cosmetic appearance of these coatings falls into four categories:

(i) metal or ceramic coatings with a shiny, metallic appearance, (ii) ceramic coatings with a white color appearance, (iii) metal oxide or ceramic coatings with a black color appearance, and (iv) paints, which can be of any color.

Decorative metallic protective coatings with a shiny cosmetic appearance  
5 include chrome and nickel. Titanium nitride is a ceramic coating which can have the appearance of brass or gold, depending on the nitrogen content in the material.

For example, Buettner, U.S. Patent No. 5,531,444 describes a golf club head coated with a hard coating of titanium nitride having a lustrous gold appearance. The titanium nitride coating is applied at a relatively high substrate temperature in the range  
10 of 650°F to 950°F (340°C to 510°C), which limits the types of golf head materials which can be coated to high softening point steels and other hard metals. Because of this requirement of high substrate temperature to achieve the desired properties of the coating, substrates which contain plastic or composite components, such as plastic putter inserts, cannot be coated.

Decorative and protective ceramic coatings with a white color appearance such as aluminum oxide, zirconium oxide, and other ceramic glazings are also known. These coatings are normally made from fine powders which are applied to the surface of components, and then fired to final form. High substrate temperatures are required to produce a durable finish, and these materials are brittle and prone to cracking and  
20 flaking when the substrate is subjected to flexure or high impact conditions.

Decorative and protective metal oxide or ceramic coatings with a black color appearance such as black chrome oxide and black aluminum oxide are also known. These coatings typically display a low-gloss black finish, which has low luster. In addition, these coatings are easily scratched by abrasives and exhibit  
25 corrosion-resistance which is less than desired.

Finally, while decorative and protective paints, which can be of any color, are widely known, such decorative and protective materials have extremely poor resistance to scratches and abrasion, and are subject to chipping and cracking when the substrate is subjected to flexure or high impact conditions.

Therefore, it is apparent that all of the prior art methods for producing  
30 decorative coatings on metal substrates suffer from one or more of the following problems:

- (1) insufficient durability and resistance to scratches and abrasion,
- (2) inadequate resistance to corrosion by environmental conditions,
- (3) limited choice of appearance color,
- (4) lack of a high luster finish,
- 5 (5) excessively high substrate temperature during application, and
- (6) inadequate adhesion to the substrate, evidenced by cracking, flaking or peeling, when subjected to flexure or high impact conditions.

The application of coating materials to the surface of articles to enhance other performance characteristics is also well known. For example, Kim, U.S. Patent No. 10 4,951,953 describes a golf club coated with a material having a high Young's modulus, or with a composite material having a high Young's modulus material as a substantial ingredient in the matrix. The coating may have a thickness in the range of about 1 to 10 mils (25 microns to 250 microns). The materials of choice have a Young's modulus of 50 million pounds per square inch (psi) or greater, and include silicon nitride, 15 aluminum oxide, silicon carbide and diamond.

#### SUMMARY OF THE INVENTION

The invention provides products having a highly durable and abrasion-resistant composite diamond-like carbon coating with controllable color which is ideally suitable as a decorative coating on metal substrates. The invention also provides the process 20 for depositing a highly adherent, highly abrasion resistant diamond-like carbon decorative coating to electrically conductive substrates. The products of the present invention include sporting equipment such as shafts and heads of golf clubs (drivers, putters, irons), cycling equipment, fishing and hunting equipment and other leisure activity products. The products of the present invention also include architectural 25 hardware and fixtures made of brass and other metals, jewelry, medical and dental instruments, writing instruments such as pens and pencils, musical instruments, eyeglass frames, cigar and cigarette lighters, automobile hood ornaments and other components, and other similar metal substrates.

The composite diamond-like carbon coating structure consists of at least a first 30 layer of Si-doped diamond-like carbon which is comprised of the elements C, H, Si and possibly O and N. An additional coating comprised of layers of Si-doped diamond-like carbon and diamond-like carbon may be applied over top of the first Si-doped

diamond-like carbon layer. The optional additional layers of Si-doped diamond-like carbon are also comprised of the elements C, H, Si and possibly O and N. The optional additional layers of diamond-like carbon are comprised of the elements C, H and possibly N.

5           The decorative and abrasion-resistant composite diamond-like carbon coating is deposited by ion-assisted plasma deposition including capacitive radio frequency plasma and ion-beam deposition, from carbon-containing and silicon-containing precursor gases consisting of hydrocarbon, silane, organosilane, organosilazane and organo-oxysilicon compounds, or mixtures thereof. The resulting decorative coating  
10 has the properties of Nanoindentation hardness in the range of approximately 5 to 35 GPa, modulus in the range of approximately 50 to 300 GPa, and thickness in the range of approximately 1 to 25 micrometers. The colors of the coating unexpectedly can be varied continuously along the spectrum of: light yellow to bronze to copper-gold to burgundy to bluish-black to black. The color range of these coatings is characterized  
15 by reflected light chromaticity coordinate values (x, y) in the range of approximately 0.25 to 0.50 for x, and in the range of approximately 0.25 to 0.45 for y as measured with Commission International de l'Eclairage ("CIE") 1931 source C standard illuminant and CIE 1931 2-degree standard observer. The preferred mode of ion-assisted plasma deposition of the decorative and abrasion-resistant diamond-like  
20 carbon coating is capacitively-coupled radio frequency (RF) plasma deposition. Optimum performance is obtained when the coating layer thickness is in the range of approximately 2 micrometers to approximately 10 micrometers.

          The elemental composition, refractive index and thickness of the composite diamond-like carbon coating are chosen to produce the desired reflected optical color.  
25 The deposition process parameters such as precursor gas composition, plasma power, pressure, and substrate bias voltage are adjusted to produce coatings with different elemental composition and refractive indexes, which change the reflected optical color, and hardness and elastic modulus, which effect the abrasion resistance and durability of the coating.

### 30                                   BRIEF DESCRIPTION OF THE DRAWING

          Further features and advantages will become apparent from the following and more particular description of the preferred embodiment of the invention, as illustrated

in the accompanying drawing in which:

FIG. 1 is a diagrammatic view, partially in cross-section, of an illustrative capacitively- coupled radio frequency plasma deposition apparatus used to manufacture coated articles of the present invention.

5           FIG. 2 is a diagrammic view, partially in cross-section of an illustrative plasma ion beam deposition apparatus used to manufacture coated articles of the present invention.

### DETAILED DESCRIPTION OF THE INVENTION

10           The present invention substantially reduces or eliminates the disadvantages and shortcomings associated with the prior art techniques by providing for the deposition of a highly durable and abrasion-resistant composite diamond-like carbon decorative coating with controllable color which is ideal for metal and other electrically  
15           conductive substrates including architectural hardware and fixtures made of brass and other metals, jewelry, medical and dental instruments, writing instruments such as pens and pencils, musical instruments, eyeglass frames, cigar and cigarette lighters,  
automobile hood ornaments and other components, sporting equipment and other products for leisure activities such as golf club shafts, golf club heads, cycling equipment, and fishing and hunting equipment, and other similar metal substrates.

20           The mechanical and optical properties of the composite diamond-like carbon coatings of the present invention can be varied over a very wide continuous range, and thus the coatings can be tailored to the needs of many diverse applications.

            The composite diamond-like carbon decorative coatings of the present invention have the following remarkable performance characteristics compared to prior art techniques:

25           (1) high durability, capable of protecting the substrate from scratches and abrasion,

            (2) resistance to corrosion by environmental conditions such as humidity, salt, and acid rain,

30           (3) high adhesion to the substrate such that cracking or flaking does not occur when the substrate is subjected to flexure or high impact conditions,

            (4) can be made with a variety of attractive colors,

            (5) can be made with high luster, or a low-luster finish if desired,

(6) can be applied at low substrate temperature, and  
(7) are amorphous and without the drawbacks of grain boundaries found in polycrystalline materials.

5 It has also been surprisingly discovered that the coatings of the present invention have a unique ability to hide fingerprints, when applied over substrates with a variety of surface finishes.

For the purposes of the present invention, the term diamond-like carbon (DLC) is meant to include amorphous materials composed of carbon, or carbon and hydrogen, whose properties resemble, but do not duplicate, those of diamond. Some of these  
10 properties are high hardness (HV = about 10 GPa to about 80 GPa), low friction coefficient (approximately less than 0.2), some transparency across the majority of the electromagnetic spectrum, and chemical inertness. At least some of the carbon atoms in DLC materials are bonded in chemical structures similar to that of diamond, but without long range crystal order. These DLC materials can contain up to 50 atomic percent of  
15 hydrogen. The diamond-like carbon materials may also contain dopant atoms such as nitrogen and silicon. For the purpose of the present invention, DLC materials which are doped with silicon in the range of approximately 2 atomic % to approximately 40 atomic % are termed Si-doped diamond-like carbon, Si-DLC. The Si-DLC materials may also contain nitrogen, and possibly oxygen.

20 The coatings of the present invention are softer and thinner than those disclosed in Kim, U.S. Patent No. 4,951,953, yet they can be remarkably resistant to scratching when deposited on steel alloys or other metals of comparable hardness. The elastic moduli of the decorative coatings of the present invention are less than the 340 GPa (50 million psi) critical value disclosed in the '953 patent, and are typically less than 200  
25 GPa (29 million psi) as measured by nanoindentation using a Nanoindenter II instrument manufactured by Nano Instruments, Incorporated (Oak Ridge, TN). Likewise, the preferred thickness range of the coatings of the present invention, in the range of approximately 1 micrometer to approximately 25 micrometers, is below the range of 25 to 250 micrometers described in the '953 patent.

30 It has been found that some coatings of the present invention have surprisingly high resistance to abrasive damage by SiC sandpaper. For example, it was found that it was very difficult to damage golf club heads which were coated with black-colored



composite diamond-like carbon decorative coatings, even by vigorous rubbing of the coated surface with 400 grit SiC sandpaper. This outstanding degree of resistance to scratching in this test was unexpected in light of the fact the SiC grit, with expected hardness of approximately 25 GPa, was substantially harder than the coatings, which had hardness in the range of approximately 17 to 20 GPa. Probable contributing factors to the outstanding scratch and abrasion resistance of the composite diamond-like carbon decorative coatings of the present invention are the very low coefficient of friction and very low chemical reactivity of the coating materials.

These composite diamond-like carbon coatings are resistant to corrosion by acids and bases, and are also excellent protective barriers against environmental corrosives such as humidity, salt, and acid rain. It was discovered, for example, that metals prone to oxidation and scaling, such as aluminum, zinc-aluminum and copper-aluminum alloys, are well protected by coatings of the present invention even during week-long exposure periods in QUV accelerated weathering tests. In these tests, the samples were exposed to alternating cycles of high intensity UV-B radiation, with peak intensity centered at 313 nm, at 50°C for 4 hours, and then water condensation at 50°C for 4 hours. These conditions produced extreme oxidation and scaling on uncoated aluminum and zinc-aluminum alloys.

The coatings of the present invention can be made with excellent adhesion to the substrate such that no delamination occurs under high impact conditions. Even on a soft material such as aluminum, which readily deformed when struck with a harder material, coatings of the present invention adhered so remarkably well that no flaking was observed in the impact area.

When applied to metal substrates, the coatings of the present invention exhibit a variety of unique and attractive colors. By adjusting the deposition parameters in the process of the present invention, the color of the composite diamond-like carbon coating can be varied continuously along the spectrum of: light yellow, bronze, copper-gold, burgundy, bluish-black, and black. The appearance of these colors on metal surfaces coated by the process of the present invention is unexpected, because a different color spectrum consisting of: nearly water-clear, light yellow, yellow-brown, brown, and black are obtained on transparent or partially transparent substrates such as

glass or plastics. Primary process parameters which control the colors of the coating are the energy of ions bombarding the surface during coating deposition, the feed gas chemistry, and the thickness of the coating.

By increasing the energetics of the deposition process, the coating color moves  
5 along the unique color spectrum of this invention from the light end, i.e. light colors, to the dark end, i.e. dark colors. The phrase "energetics of the deposition process," is defined as the energy delivered to the coating surface divided by the deposition rate. Energy is delivered to the coating surface by substrate heating, impacting ions and fast neutral species, and radiated power from the plasma. For the ion-assisted plasma  
10 deposition process of the present invention, the energetics of the deposition process can be increased by increasing any of the following independent process control parameters while holding others constant: (i) the power, e.g. RF power, applied to the plasma, (ii) the vacuum system pumping speed, (iii) the area ratio of the grounded electrode to the powered electrode, and (iv) the substrate temperature, by increasing the electrode  
15 temperature. For the ion-assisted plasma deposition process of the present invention, the energetics of the deposition process can be increased by decreasing the following independent process control parameters while holding others constant: (v) the total flow rate of process gases, (vi) the flow rate of the precursor feed gases, (vii) the molecular weight of the precursor feed gas, and (viii) the electrically active surface area of the  
20 powered electrode and substrates.

DLC materials made from a pure hydrocarbon precursor feed gases are black in color, when deposited to thicknesses greater than about 1 micrometer, but the color can be shifted to the light end of the spectrum, i.e. yellow-brown color, by reducing the energetics of the deposition process. However, for coatings greater than approximately  
25 1 micrometer which are made from hydrocarbon precursors only, the color shifts to the yellow-brown range at such low deposition energy that the resulting coatings are soft and polymeric in nature, and unsuitable for protecting metal substrates from abrasion.

It has unexpectedly been found that for the coatings of the present invention containing Si-DLC, the coating color can be controlled by selectively adjusting the  
30 precursor feed gas chemistry. It has been found that a color shift toward the light end of the spectrum can be induced in the coating under conditions of high deposition energetics by adding silicon to the carbon-containing precursor feed gas stream.

Appropriate sources of silicon for the process of the present invention include, but are not limited to silanes, organosilanes, organosilazanes, and organo-oxy silicon compounds such as organosiloxanes. Examples of silicon-containing compounds suitable for the process of the present invention include, but are not limited to silane, disilane, diethylsilane, tetramethylsilane, hexamethyldisilazane, hexamethyldisiloxane, tetramethyldisilazane, tetramethyldisiloxane, octamethylcyclotetrasiloxane, and ethoxytrimethylsilane. Suitable carbon-containing precursors for DLC include, but are not limited to hydrocarbons such as methane, butane, acetylene and cyclohexane, and mixtures thereof. These carbon-containing precursors may be used alone or in conjunction with noble gases, hydrogen or nitrogen for the deposition of DLC, or combined with the silicon-containing precursor gases for the deposition of Si-DLC. When silicon-containing and carbon-containing precursor feed gases are used in the process of the present invention, the coating color can be further shifted toward the light end of the spectrum by adding nitrogen, oxygen or hydrogen to the precursor feed gas stream.

The absorption of light in DLC materials is typically explained in the prior art by the presence of an extensive  $sp^2$  carbon-carbon bonding network. The inventors speculate that the presence of bonded Si atoms in the coatings of the present invention shifts the coating color toward the light end of the spectrum by effectively diluting the carbon concentration in the coating, and thereby hindering the formation of this long-range  $sp^2$  carbon-carbon network. Bonded nitrogen atoms in the diamond-like carbon material may produce a similar effect. The inventors also speculate that the presence of oxygen or hydrogen further reduces the carbon concentration in the coating, by reacting with the carbon in the feed gas and in the coating and thereby producing highly volatile, stable and unreactive carbon byproducts (such as methane and carbon dioxide) that can be readily removed from the deposition chamber by the vacuum pump. Additionally, since oxygen atoms readily bond with silicon, when oxygen is present in the deposition process gas it may reactively bond into the Si-DLC matrix of the coatings of the present invention. Since there is no absorption of visible light associated with Si-O or C-O bonds, as the oxygen content in the coating is increased, the coating color is shifted toward the lighter end of the spectrum.

On metals having mirror-like surface finishes, the coatings of the present invention

which contains Si-DLC exhibit an unusual luster and depth of color. When viewed at different angles, the coatings can appear to shift in color. When viewed in sunlight, the depth of color is accentuated, and the appearance of the coating can be very different than in artificial light. This effect is also noticeable at the dark end of the color spectrum, where shades of purple and blue can be seen in the coatings at certain viewing angles. DLC coatings made from pure hydrocarbon precursor feed gases at high energy are also shiny black in color, but lack the luster achieved by the composite diamond-like carbon decorative coatings of the present invention which contain silicon.

The coatings of the present invention can be produced at low substrate temperatures of less than 150°C, whereas coatings of the prior art generally require substrate temperatures greater than 300°C. This enables deposition of the composite diamond-like carbon coatings on temperature sensitive alloys and metals, as well as on composite articles with temperature sensitive components, such as plastic golf putter inserts. In addition, the low deposition temperature capability of the process of the present invention means that no special fixturing concepts, such as direct contact water cooling of the substrates are required.

It has also been found that the process of the present invention can be used to deposit thick and highly durable coatings at substrate temperatures less than 150°C, without intimate thermal contact between the substrate and a cooled surface. This is particularly important for applications where the majority of the surface area of a substrate needs to be coated, and therefore cannot be placed in intimate contact with a cooled mounting surface. Furthermore, this capability greatly simplifies the fixturing requirements for temperature sensitive substrates with complex shapes.

Accordingly, it was discovered that the maximum substrate temperature reached, in the deposition process of the present invention, declines significantly when the pressure within the deposition vacuum chamber is decreased below the typical range of  $50 \times 10^{-3}$  Torr to  $500 \times 10^{-3}$  Torr employed in prior art RF plasma deposition of DLC coatings. This decrease in substrate temperature was highly unexpected, because the total power required to deposit coatings of equal thickness and hardness at different pressures is approximately constant. It has been found that as the process pressure is decreased, less power is required to maintain the desired substrate bias voltage, but this effect is offset by a reduction in the deposition rate. The observed effect of reduced substrate

temperature is too dramatic to be explained by the increased effectiveness of radiative cooling when the instantaneous heat load is low. The inventors have observed that the low pressure deposition plasma is more diffuse than the prior art plasmas, and it is speculated that at low pressures, the plasma power may be dissipated more evenly at the boundaries of the plasma.

The coatings of the present invention are amorphous, unlike the coatings on golf clubs described by Kim in the '953 patent. In crystalline coatings of the prior art, the presence of grain boundaries and other imperfections degrades the ability of the coating to protect the substrate from corrosive agents, reduces the ability of the coating to withstand impact and flexure without cracking, chipping, or flaking from the substrate. In addition, the surface morphology of crystalline coatings necessitates post-deposition polishing to achieve a mirror-like appearance. For the coatings of the present invention applied to smooth substrates, no post-deposition processing is required to achieve the attractive, lustrous surface finish.

For the present invention, it is preferred that the thickness of the composite diamond-like carbon coating be greater than approximately 1 micrometer, which is much greater than the wavelengths of visible light (approximately 0.5 micrometer). In this case, the perceived color of the coating is significantly influenced by the inherent optical color (a combination of absorption, reflection and refractive index characteristics) of the coating material, and the reflectivity characteristics of the substrate. For the case of the present invention, the perceived color of the coating is not simply generated by thin film optical interference effects, known to those skilled in the art of optical coatings. Representative of prior art thin film optical interference coatings are quarter wavelength stacks of dielectric layers, which may be combined with thin reflective metal films, to generate iridescent colors on substrates such as sunglass lenses.

For cases where the attenuation of the light through the coating, via absorption, is so strong that reflected light from the coating-metal interface is imperceptible, the coating can have a shiny appearance, but lacks the luster or depth of more transparent coatings. For hard DLC materials, the threshold coating thickness for complete absorption is approximately 0.5 micrometer, and above this threshold, these coatings are black. As the absorption coefficient is reduced, by reducing the deposition

energetics or by changing the precursor feed gas chemistry as described above, the maximum thickness for which the luster is apparent increases.

There are several composite diamond-like carbon coating structures in the present invention that provide the lustrous appearance described above, as well as other performance benefits. The composite diamond-like carbon decorative coatings have hardness in the range of approximately 5 to 35 GPa, and modulus in the range of approximately 50 GPa to 300 GPa.

In the first composite diamond-like carbon coating structure which provides a lustrous appearance, a single layer of transparent or partially transparent Si-DLC is deposited on a metal substrate to a thickness in the range of 1 to 25 micrometers. In addition to Si, C and H, the Si-DLC may also contain O and N. By controlling the deposition energetics, the precursor feed gas chemistry, and the thickness of the coating in the range of approximately 1 to 25 micrometers, lustrous colors can be achieved along the color spectrum defined by light yellow, bronze, copper-gold, burgundy, bluish-black and black.

In the second composite diamond-like carbon coating structure which provides a lustrous appearance, multiple layers of transparent or partially transparent Si-DLC of different elemental composition are sequentially deposited on the metal substrate. In addition to Si, C and H, all layers in this coating may also contain O and N. The coating structure can be tailored to the requirements of the application. For example, the first layer may be enriched with silicon in order to maximize the adhesion to the substrate. Alternately, several thin layers with varying refractive indices may be included at the top of the coating (away from the coating-metal interface) in order to control or reduce any thin film interference effects that may be present.

In the third composite diamond-like carbon coating structure which provides a lustrous appearance, a coating is produced by first depositing on a metal substrate one or more layers of the transparent or partially-transparent Si-DLC, containing Si, C, H and optionally O and N, and then depositing at least one layer of DLC, consisting essentially of C and H, and optionally N. The thickness of the single DLC layer, or multiple DLC layers, is less than the maximum for complete absorption of visible light within the composite coating, and the total thickness of the composite coating is in the range of approximately 1 to 25 micrometers. The third composite diamond-like carbon

coating structure has the advantage that the composite coating with the DLC top layer generally affords maximum chemical resistance, with the exception of oxidizing environments, for which the Si-DLC top layer is preferred. The DLC layers in this structure may be further refined to suit the mechanical requirements of the application by adding small amounts of other elemental constituents. For example, small amounts of metal may be incorporated in the top DLC layer to reduce the friction of the coating in high humidity environments.

In the fourth composite diamond-like carbon coating structure which provides a lustrous appearance, a nontransparent layer of DLC, consisting essentially of C, H and optionally N, is deposited between layers of transparent Si-DLC, consisting of Si, C, H, and optionally O and N. The purpose of the Si-DLC layer adjacent to the metal interface is to provide good adhesion, while the purpose of the top layer of Si-DLC is to provide luster and depth of color to the coating. While visible light entering the DLC layer or layers is completely absorbed, some of the light impinging on the interface between the Si-DLC and the DLC is reflected due to refractive index mismatch. The advantage of the fourth composite diamond-like carbon coating structure is that a shiny black coating with luster and depth of color is produced.

Finally, a highly durable shiny black composite diamond-like carbon decorative coating having a structure of a first layer of Si-DLC consisting of Si, C, H, and optionally O and N, and at least a second layer of DLC consisting essentially of C, H and optionally N, which DLC layer is thick enough and of sufficient optical density to not allow visible light to reach the Si-DLC layer can be made by the ion-assisted plasma deposition process of the present invention. The top layer of DLC in this structure has a thickness of greater than 0.5 micrometer, and the total thickness of the composite coating is in the range of approximately 1 to 25 micrometers. This type of composite diamond-like carbon coating has the properties of outstanding adhesion, superior abrasion resistance, corrosion resistance, but has a shiny black color, rather than the lustrous colors of the Si-DLC containing coatings of the present invention. In addition, these shiny black composite diamond-like carbon coatings can have high hardness in the range of approximately 15 to 35 GPa, and high modulus, in the range of approximately 120 GPa to 300 GPa, both of which are at the upper end of the range of these properties for the coatings of the present invention. The characteristics and appearance

of this shiny black composite diamond-like carbon decorative coating is ideal for sporting equipment including golf club shafts, and golf club heads such as putters, drivers and irons.

5 It has been found that deposition of the first layer of Si-DLC material, having a Si concentration between approximately 2 atomic percent and 40 atomic percent prior to the deposition of a DLC layer, results in highly adherent composite diamond-like carbon decorative coatings with outstanding adhesion to the substrate and outstanding abrasion-resistance properties. It is currently believed that reaction between the Si atoms in the Si-DLC layer and the substrate is critical for the composite diamond-like carbon coating to exhibit excellent adhesion to the substrate. It is currently believed  
10 that reaction between the Si atoms in the Si-DLC layer and the carbon atoms in the DLC layer is critical for the outstanding adhesion between these two layers.

For structures in which a second coating, consisting of at least one additional layer of DLC or Si-DLC, is deposited on top of the first Si-DLC layer, the thickness of the  
15 first Si-DLC layer is in the range of approximately 0.1 to 15 micrometers. This thickness range has been found to produce the best adhesion to the substrate for the multiple-layer coatings of the present invention.

The preferred method of the present invention comprises the following steps. The substrate is first chemically cleaned to remove contaminants. In the second step, the  
20 substrate is inserted into a vacuum coating chamber and the air in the chamber is evacuated. Next, in the third step, the substrate surface is sputter-etched by a flux of energetic ions or other reactive species to assist in the removal of residual contaminants such as residual hydrocarbons and surface oxides, and to activate the surface. In the fourth step, after the substrate surface has been etched and activated, at least a first  
25 layer of Si-DLC is deposited by an ion-assisted plasma deposition process, preferably capacitively-coupled RF plasma deposition, from carbon-containing and silicon-containing precursor gas compounds. Upon completion of the formation of the Si-DLC first coating layer, an additional coating, consisting of at least one layer of DLC or Si-DLC may be deposited by an ion-assisted plasma deposition process, preferably  
30 capacitively-coupled RF plasma deposition, from precursor gases. The deposition of the desired thickness and number of DLC and Si-DLC layers, is continued until the desired optical color and total coating thickness is achieved, at which point the



deposition process on the substrates is terminated. Then, the vacuum chamber pressure is increased to atmospheric pressure, and the coated metal substrates having a highly durable and abrasion-resistant composite diamond-like carbon decorative coating are removed from the vacuum chamber.

5 It is understood that the process of the present invention can be carried out in a batch-type vacuum deposition system, in which the main vacuum chamber is evacuated and vented to atmosphere after processing each batch of parts; a load-locked deposition system, in which the main vacuum deposition chamber is maintained under vacuum at all times, but batches of parts to be coated are shuttled in and out of the deposition zone  
10 through vacuum-to-air load locks; or in-line processing vacuum deposition chambers, in which parts are flowing constantly from atmosphere, through differential pumping zones, into the deposition chamber, back through differential pumping zones, and returned to atmospheric pressure.

It is possible to perform ion-assisted plasma deposition of DLC materials using a  
15 variety of methods, including capacitively-coupled RF plasma deposition, DC plasma deposition, ion beam plasma deposition and ion-assisted sputter deposition. However, since the decorative coatings of the present invention are ideally suited to a variety of substrates with highly curved surfaces, the RF plasma or DC plasma deposition methods are preferred with the RF plasma method most preferred. It is known that properties of  
20 DLC materials deposited by direct ion beam deposition are very sensitive to the angle of incidence of the ion beam onto the substrate. At incident angles in the range of approximately 60 degrees to 90 degrees, highly smooth, dense and hard DLC films are deposited. However, when the ion beam is directed onto the substrate at a grazing angle of incidence less than approximately 45 degrees, the films become rougher, and  
25 the density and hardness decrease. This effect becomes much worse as the angle of incidence approaches 0 degrees. Therefore, complex fixturing is required for obtaining uniform DLC materials of optimum quality on highly curved surfaces, such as golf club heads, using ion beam deposition. For the case of ion-assisted sputter deposition of  
DLC and Si-DLC coatings, the deposition rate of these materials is typically much  
30 lower than that achieved by capacitively-coupled RF plasma deposition. In addition, complex fixturing is required for obtaining uniform diamond-like carbon materials of optimum quality on highly curved surfaces, such as golf club heads, using ion-assisted

sputter deposition.

5 A preferred ion-assisted plasma deposition apparatus for producing the preferred embodiment of the present invention by capacitively-coupled RF plasma deposition, in accordance with Holland, U.S. Patent No. 4,382,100, which is incorporated herein by reference, is illustrated schematically in FIG. 1. The process is carried out inside vacuum chamber 10, which is fabricated according to techniques known in the art. Vacuum chamber 10 is evacuated by first pumping with a rough vacuum pump (not shown) and then by an optional high vacuum pump (not shown). Use of a high vacuum pump allows for removal of greater levels of air and contaminants from the chamber prior to initiating the deposition process, and also enables operation of the plasma at lower pressures than can be achieved with a rough vacuum pump. The high vacuum pump can be a diffusion pump, turbomolecular pump, or other high vacuum pumps known in the art.

15 Within electrically grounded metal vacuum chamber or glass vacuum chamber 10 with electrically grounded electrode 12, substrates 13 (for example, golf club heads, as shown) are mounted either in recessed holes directly in the powered electrode, or equivalently in recessed holes 14 in electrically conductive mounting block 15 which in turn rests on powered electrode 20. Alternatively, substrates 13 may be mounted on metal mounting studs 16, which are in electrical contact with powered electrode 20 and may or may not be recessed into mounting block 15. Powered electrode 20 may be stationary, or may incorporate a rotation mechanism. Powered electrode 20 is shown with cooling water inlet 22 and cooling water outlet 24 of a typical cooling system 25 for RF chamber 10. RF power circuit 30 is electrically connected to grounded electrode 12 and powered electrode 20 via cables or connectors as shown by means well known in the art. Electrically grounded dark space shield 32 is separated from powered electrode 20 by a small gap 34. DC blocking capacitor 36 in RF power circuit 30 allows the entire electrode assembly, i.e., substrates 13, mounting block 15, mounting studs 16, and powered electrode 20, to develop a negative voltage (also known in the art as DC self-bias voltage) upon ignition of plasma 37 by application of suitable RF power from RF generator 38 in the presence of process gases. The process gases, which may include argon for sputter-etching of the substrates prior to coating deposition, and precursor gases for deposition, pass through gas line 40 into shower

head distributor 42 and out through orifices 44 into chamber 10. The effluent gases are exhausted through exhaust pumping port 50. An automated variable throttle valve in the exhaust port (not shown in FIG. 1) is used to control the rate of gas removal from the vacuum chamber. The pressure in the chamber is thus controlled by throttle valve position and total gas flow into the chamber. RF blocking inductor 52 in circuit 30 permits measurement of the DC bias voltage via voltmeter 54. Matching network 56 in circuit 30 is tuned to assure optimum delivery of RF power into plasma 37. Typical process operating conditions include gas pressure in the range of approximately  $1 \times 10^{-3}$  Torr to  $500 \times 10^{-3}$  Torr, RF frequency of 13.56 MHz, peak-to-peak RF voltages in the range of approximately 500 to 2000 Volts, and DC self-bias voltages in the range of approximately -100 to -1,000 Volts.

In capacitively-coupled RF plasma systems such as that illustrated in FIG. 1, the surface area of grounded surfaces is normally substantially larger than the surface area of powered electrode 20 and substrates 13. In such asymmetric systems, ion bombardment energies and fluxes are much larger on the powered electrode than they are on the grounded surfaces including grounded electrode 12. Bombardment by positive ions from an inert gas (e.g. Ar) plasma results in sputter-etching of the exposed surfaces of the substrate assembly which includes substrates 13, mounting block 15, mounting studs 16, and powered electrode 20. Likewise, ion bombardment by positive ions of the precursor gases, such as hydrocarbon gases (e.g. methane, acetylene, butane, cyclohexane, etc.), results in deposition of a DLC coating on all exposed surfaces of the substrate assembly, including substrates 13, mounting block 15, mounting studs 16 and powered electrode 20.

Deposition on the edges and backside of the powered electrode is commonly avoided in capacitive RF plasma systems by the use of dark space shield 32 shown in FIG. 1. As illustrated, grounded metal shield 32 is separated from powered electrode 20 by thin vacuum gap 34. Gap 34 is thinner than the width of the plasma dark space adjacent the exposed surface of powered electrode 20, and thus a self-sustaining plasma will not develop in gap 34.

Additionally, it is possible to employ the electronic masking method of Petrmichl et al., U.S. Patent No. 5,653,812, which is incorporated herein by reference to minimize deposition of coating onto mounting block 15 and on other surfaces inside chamber 10

where deposition is undesirable.

Finally, it is also possible to mount the metal substrates to be coated on a vertical powered electrode assembly (not shown). In this configuration, many individual substrates are attached to metal mounting poles which connect to a common center post, much like the branches on a pine tree connect to the tree trunk. The center post is an intimate part of the powered electrode assembly. This configuration is commonly referred to as a "Christmas tree" configuration in the prior art, and has advantages of higher substrate packing density compared to the horizontal fixturing arrangement shown in FIG. 1.

The apparatus of FIG. 1 may also be used to perform DC plasma deposition by replacing RF power circuit 30 with a DC power supply. In this configuration, the negative terminal of the DC power supply is connected to electrode 20, and a DC plasma is ignited between the substrates and the grounded components such as electrode 12 within vacuum chamber 10. DC power supplies capable of negative bias voltages up to -3000 Volts are suitable for the DC plasma deposition method. The advantage of the DC plasma method of ion-assisted plasma deposition is the simplicity of the power supply configuration. However, this configuration is susceptible to formation of arcs during the deposition of insulating Si-DLC and DLC coatings. The arcs may be overcome by using arc suppression method known in the art.

In the ion-assisted plasma deposition process carried out in an apparatus such as that illustrated in FIG. 1, the primary control parameters are the precursor composition and flow rate, the bias voltage, and the substrate temperature. The useful range of the latter is, however, limited for metal alloy substrates of low melting point or softening point, and substrates which contain temperature sensitive components, such as plastic inserts which are used in golf putters. Other process parameters that affect the coating properties in the ion-assisted plasma process are the total flow rate, discharge power, pressure, size and shape of electrodes, and the presence of external magnetic fields.

Alternatively, the apparatus illustrated in FIG. 2 may be utilized to perform the ion-assisted deposition process of the present invention by plasma ion beam deposition. As shown in FIG. 2, the process is carried out inside vacuum chamber 61, which is pumped by high vacuum pump 62 which is typically a turbomolecular pump or diffusion pump. Fixture 63 is used to hold substrates 71, in this case on rotating drum 70. As illustrated

in FIG. 2, drum 70 and substrates 71 both rotate in opposite directions, but the type and degree of substrate rotation is chosen depending on the configuration of the substrates, to obtain adequate uniformity of the coating thickness and properties. Deposition of the Si-DLC and DLC layers is carried out by ion plasma beam deposition using ion source  
5 64, which is operated on inert gases introduced via inlet 65, and silicon-containing and carbon-containing precursor gases which may be introduced via inlets 66 or 67. Inlets 68 and 69 are available for adding dopant gases such as oxygen, nitrogen and hydrogen to the chamber during deposition to modify the properties of the depositing Si-DLC or DLC layer. An example of the use of FIG. 2 for the decorative coatings of the present  
10 invention would be in the coating of golf club shaft substrates 71, mounted on rotating spindles 70 of drum planetary fixture 63. The long axis of the golf club shafts would be perpendicular to the plane of the drawing of FIG. 2.

Additionally, ion source 64 could be replaced by a magnetron sputtering cathode to perform deposition of the coatings of the present invention by ion-assisted sputter  
15 deposition. In this case, the carbon-containing and silicon-containing deposition flux is achieved by sputtering from carbon-containing and silicon-containing cathode materials such as carbon, silicon, and silicon carbide.

According to the method of the present invention, the substrate is first chemically cleaned to remove contaminants, such as residual hydrocarbons and other contaminants,  
20 from the substrate manufacturing and handling processes. Ultrasonic cleaning in solvents, or other aqueous detergents as known in the art is effective. Details of the cleaning procedure depend upon the nature of the contamination and residue remaining on the part after manufacture and subsequent handling. It has been found that it is critical for this chemical cleaning step to be effective in removing surface contaminants  
25 and residues, or the resulting adhesion of the coating will be poor.

In the second step of the process, the substrate is inserted into a vacuum chamber, and the air in the chamber is evacuated. The vacuum chamber is then typically  
evacuated to a pressure of approximately  $1 \times 10^{-3}$  Torr or less. The exact level of  
vacuum is dependent upon the nature of the substrate material, the sputter-etching rate  
30 of the substrate, the constituents present in the vacuum chamber residual gas, and the details of the coating process. It is not desirable to evacuate to lower pressures than necessary, as this increases the overall process cycle time, and reduces the throughput

of the coating system.

In the third step of the process, non-depositing gases such as argon, xenon, krypton, nitrogen and hydrogen are flowed into the chamber, and a plasma is initiated by applying RF power to the substrates. Ions in the plasma are extracted by the bias  
5 voltage on the substrates, and impact the substrate with sufficient energy to sputter-etch the substrate surface to remove residual contaminants, such as hydrocarbons, surface oxides and other unwanted materials not removed in the first cleaning step, and to activate the surface. This sputter-etching of the substrate surface generates an atomically clean surface, and is required to achieve high adhesion between the substrate  
10 surface and the coating. Typically, in order to achieve efficient and rapid ion sputter-etching, the bias voltage is set to -500 V or more, and the chamber pressure is maintained as low as possible (less than approximately  $50 \times 10^{-3}$  Torr) by completely opening the automated throttle valve in the exhaust port. Bias voltages as high as approximately -2000 Volts can be used, but lower bias voltages are usually used in  
15 order to minimize heating of the substrate.

In the fourth step of the process, immediately after the substrate surface has been sputter-etched, at least a first layer of Si-DLC is deposited by ion-assisted plasma deposition, preferably capacitively-coupled RF plasma deposition, from carbon-containing and silicon-containing precursor gases which are introduced into the  
20 vacuum chamber. These carbon-containing and silicon-containing precursor gases consist of hydrocarbon, silane, organosilane, organosilazane and organo-oxysilicon compounds, or mixtures thereof. The flow of non-depositing gas or gases used to sputter-etch the substrate may be shut off entirely at this point in the process, or alternatively, may continue along with the flow of precursor gases. Other gases, such  
25 as nitrogen, hydrogen or oxygen, may be added to the precursor gas flow in order to modify the optical and mechanical properties of the depositing Si-DLC coating.

Upon completion of the deposition of the Si-DLC first coating layer, a second coating consisting of at least one layer of DLC or Si-DLC may be deposited by ion-assisted plasma deposition, preferably capacitively-coupled RF plasma deposition,  
30 from precursor gases. DLC is deposited from hydrocarbon precursor gases, and possibly nitrogen, hydrogen, and inert gases. Additional layers of Si-DLC are deposited from carbon-containing and silicon-containing precursor gases, including hydrocarbon,

silane, organosilane, organosilazane and organo-oxysilicon compounds, or mixtures thereof. Other gases, such as nitrogen, hydrogen or oxygen, may be added to the precursor gas flow in order to modify the optical and mechanical properties of the additional layers of Si-DLC.

5       The thickness, refractive index, and number of the layers in the composite coating are chosen to produce the desired optical color, as well as the required durability characteristics such as resistance to scratches and abrasion. The physical thickness of individual layers in the second coating is typically approximately 0.5 micrometer or greater. If a shiny black coating is desired, the thickness of the DLC layer in the second  
10       coating is greater than 0.5 micrometer. Optimally, the additional layer of DLC or Si-DLC is deposited immediately after completion of the first coating layer, in the same vacuum chamber and in the same vacuum cycle. This eliminates the added cost of additional pumpdown cycles, and improves the quality of the interface between the first coating layer and the second coating.

15       The deposition of the desired thickness and number of DLC and Si-DLC layers is continued until the desired optical color and total coating thickness in the range of approximately 1 to 25 micrometers is achieved, at which point the deposition process on the substrates is terminated. Then, the vacuum chamber pressure is increased to atmospheric pressure, and the substrates having a highly durable and abrasion-resistant  
20       composite diamond-like carbon decorative coating having thickness in the range of approximately 1 to 25 micrometers, hardness in the range of approximately 5 to 35 GPa, and modulus in the range of approximately 50 to 300 GPa is removed from the vacuum chamber.

      Appropriate types of precursor feed gases for the process for depositing the  
25       decorative composite diamond-like carbon coatings of the present invention include, but are not limited to hydrocarbon compounds, silanes, organosilanes, organosilazanes, and organo-oxysilicon compounds such as organosiloxanes. Examples of specific compounds suitable for the process of the present invention include, but are not limited to carbon-containing precursors such as methane, butane, cyclohexane and acetylene,  
30       and silicon-containing precursors such as silane, disilane, diethylsilane, tetramethylsilane, hexamethyldisilazane, tetramethyldisilazane, hexamethyldisiloxane, tetramethyldisiloxane, and ethoxytrimethylsilane. Noble gases such as argon, krypton

and xenon, and other gases such as nitrogen, oxygen and hydrogen may be added to the flow of precursor gases to modify the properties of the depositing coatings. Note that some of the silicon-containing precursors such as diethylsilane and tetramethylsilane also contain carbon atoms, some of the silicon-containing precursors such as  
5 hexamethyldisilazane and tetramethyldisilazane also contain C and N atoms, and some of the silicon-containing precursors such as hexamethyldisiloxane, tetramethyldisiloxane, and ethoxytrimethylsilane also contain C and O atoms.

The examples which follow illustrate the superior performance of the method of this invention. The examples are for illustrative purposes only and are not meant to limit the  
10 scope of the claims in any way.

#### Example A

Golf club shafts and shafts with attached heads including a driver and iron all made of steel and other metal alloys, including a driver and iron, were coated with shiny  
15 black, highly durable, highly abrasion-resistant and corrosion-resistant decorative composite diamond-like carbon coatings by ion-assisted plasma deposition. The coatings were deposited in a capacitively-coupled RF plasma deposition apparatus, consisting of a 24-inch diameter x 36-inch high vacuum chamber with a 6-inch diameter water-cooled powered electrode. The vacuum chamber was evacuated by a roots  
20 blower/mechanical pump combination, and a turbomolecular high vacuum pump. The golf clubs, including shafts and heads, were cleaned by wiping with isopropyl alcohol, allowed to dry, and then were mounted vertically, with the handle end attached to the powered electrode by a simple metal mounting stud. Individual golf club shafts and golf club shafts with attached heads were coated one at a time.

25 The chamber was evacuated to less than  $1 \times 10^{-3}$  Torr, and then argon was introduced at a flow of 25 sccm and the pressure increased to  $22 \times 10^{-3}$  Torr. A plasma was initiated by applying RF power to the powered electrode and golf club, and the RF power was increased to 360 W until a -625 V substrate bias was achieved. The golf clubs were sputter-etched in the argon plasma for 3 minutes, before 25 sccm of  
30 tetramethylsilane was added to the argon gas flow. The pressure increased to  $28 \times 10^{-3}$  Torr, and the power was increased to 400 W to maintain the -625 V bias. In the following 10 minutes, a first layer of Si-DLC was deposited from the



tetramethysilane/argon mixture to a thickness of about 0.5 micrometer. Next, 25 sccm cyclohexane was introduced, and the argon and tetramethysilane flows were both shut off, to initiate the deposition of DLC. The pressure decreased to  $27 \times 10^{-3}$  Torr, and the power was adjusted to 390 W to maintain the -625 V bias. The DLC deposition was continued for a total of 30 minutes, to achieve a top layer of DLC which was approximately 2 micrometers thick. Then, the RF power and the cyclohexane flow was then turned off, the chamber was vented, and the coated golf clubs were removed. The coated golf club shafts and heads had a uniform shiny black appearance, and were highly resistant to scratching with 400 grit SiC sandpaper.

#### Example B

Golf club putters and coupons made of several different metals were coated by the ion-assisted plasma deposition method of the present invention, using a variety of process conditions to generate highly adherent and durable composite diamond-like carbon coatings with a variety of colors. All of the coating deposition runs were carried out in the same coating chamber used in Example A. The metal coupons were prepared with several surface finishes: mirror-polished, a "satin" machined finish, an as-machined finish and a bead-blasted finish.

All of the substrates were chemically cleaned in an aqueous soap solution in an ultrasonic bath, then rinsed with isopropyl alcohol, air dried, and then mounted onto the powered electrode. Putters were attached to the powered electrode via a mounting stud as illustrated in FIG. 1. Metal coupons were attached to the side of an aluminum mounting block, which simulated the shape of a golf club putter, which was attached to powered electrode. After evacuation of the air in the vacuum chamber to a pressure of less than  $1 \times 10^{-3}$  Torr, argon gas was introduced into the chamber at a flow rate of 90 sccm, to produce a pressure of approximately  $20 \times 10^{-3}$  Torr. A plasma was ignited at a RF frequency of 13.56 MHz, and a power of approximately 400 Watts, resulting in a self-bias voltage of -700 Volts on the powered electrode and the substrates. The substrates were sputter-etched for a period of 10 minutes under these conditions to remove residual hydrocarbon contamination and oxide layers from the surface. Then, composite diamond-like carbon coatings containing at least one layer of Si-DLC were deposited using ion-assisted plasma deposition from silicon-containing precursor gases, using the conditions presented in Table 1 below. Properties of the deposited composite

diamond-like carbon coatings on polished aluminum, ZA12 zinc-aluminum alloy, and stainless steel substrates are also summarized in Table 1.

5 The hardness and modulus values for each of the coatings presented in Table 1 were obtained by nanoindentation using a Nano Instruments, Incorporated (Oak Ridge, TN) Nano II nanoindenter. A Berkovich style indentation tip was used. Indents were made at three depths: 50 nm, 100 nm, and 150 nm. The reported hardness and modulus values are the average of five indents at each of the three depths. A Si (100) single crystal standard (hardness 10.5 GPa) was used to calibrate the instrument.

Table 1 (cont'd)

<u>Run No.</u>	<u>Flow Rate and Precursor; Bias Voltage for Si-DLC First Layer</u>	<u>Si-DLC First Layer Thickness (microns)</u>	<u>Flow Rate and Precursor; Bias Voltage for Second Layer</u>	<u>Second Layer Thickness (microns)</u>	<u>Coating Hardness; Modulus (GPa)</u>	<u>Color</u>
16	100 sccm TMS + 25 sccm Ar; -300 V	3.4	None	----	8.5; 68	Lustrous burgundy
9	100 sccm TMS + 25 sccm Ar; -500 V	3.7	None	----	14; 118	Lustrous bluish-black
5	100 sccm TMS + 25 sccm Ar; -700 V	5.9	None	----	17; 153	Lustrous bluish- black
32	25 sccm HMDSN; -500 V	3.6	None	----	7.7; 62	Lustrous copper- gold

Table I (cont'd)

31	25 sccm HMDSN; -700 V	3.6	None	---	11; 93	Lustrous burgundy
28	25 sccm TMDSN + 25 sccm Ar; -700 V	3.1	None	---	9.7; 86	Lustrous copper- gold
24	25 sccm TMDSN + 25 sccm Ar; -700 V	5.4	None	---	8.0; 68	Lustrous copper- gold
30	25 sccm TMDSN + 25 sccm Ar; -700 V	0.6	100 sccm cyclohexane; -500 V	1.7	13.5; 110	Shiny black
27	100 sccm TMDSN + 25 sccm Ar; -700 V	2.5	100 sccm cyclohexane; -700 V	0.7	17.2; 137	Shiny black

Note: TMS = tetramethylsilane; HMDSN = hexamethyldisilazane;  
TMDSN = tetramethyldisilazane.

The coatings presented in Table 1 demonstrated excellent adhesion in boiling water-to-ice water thermal shock adhesion tests, and in impact tests in which the coated substrates were impacted with a sharp corner of a hard metal wedge golf club head, to simulate aggressive banging together of unprotected golf club heads.

- 5           Reflected light chromaticity coordinates of the coupons were measured using a Hunter UltraScan XE dual beam, xenon source, flash spectrophotometer with a wavelength range of 360 to 750 nm. A six-inch diameter, barium coated integrating sphere was used to measure reflected light. Tristimulus integrations using CIE 1931 source C standard illuminant and CIE 1931 2-degree standard observer were performed
- 10           to obtain the chromaticity coordinates were based on a triangular bandpass of 10 nm and a wavelength interval of 10 nm. The appearance color, and chromaticity coordinate data for the test coupons are presented in Table 2 below.

Table 2 (cont'd)

Run No.	Coating Hardness; Modulus (GPa)	Appearance <u>Color</u>	Chromaticity Values of coated		Chromaticity Values of coated SS coupon (Y, x, y)
			Al coupon (Y, x, y)	SS coupon (Y, x, y)	
5	16	Lustrous burgundy	20.4, 0.375, 0.338	17.0, 0.354, 0.328	
	9	Lustrous bluish-black	18.7, 0.323, 0.311	17.3, 0.310, 0.310	
10	15	Lustrous bluish-black	19.71, 0.305, 0.311	18.7, 0.306, 0.312	
	32	Lustrous copper-gold	28.6, 0.406, 0.378	21.9, 0.382, 0.356	
	31	Lustrous burgundy	20.3, 0.376, 0.338	18.6, 0.350, 0.326	
15	28	Lustrous copper-gold	23.8, 0.392, 0.353	20.2, 0.372, 0.344	

Table 2 (cont'd)

24	8.0; 68	Lustrous copper-gold	24.0, 0.408, 0.364	19.8, 0.395, 0.356
30	13.5; 110	Shiny black	13.8, 0.316, 0.323	14.9, 0.312, 0.318
5	27	17.2; 137	15.2, 0.313, 0.319	15.8, 0.313, 0.319

Note: SS = stainless steel coupon.

From examination of the data in Table 2, it is apparent that the shiny black composite diamond-like carbon decorative coatings with a DLC top layer deposited in Run No. 27 and 30 have the lower values of Y than do all of the other coatings which have Si-DLC as the top layer. For the case of the coatings from Run No. 27 and 30, the values of Y were 15.2 and 13.8, respectively, whereas for all the other coatings which have Si-DLC as the top layer, the values of Y were between 18 and 29. This indicates that the coatings with the Si-DLC top layer are more reflective than the coatings with a DLC top layer which is greater than 0.5 micrometer thick. Therefore, the Si-DLC coatings appear to have higher luster, i.e. are lustrous, than do the coatings with a DLC top layer which is greater than 0.5 micrometer thick.

The chromaticity coordinate values of (x,y) in Table 2 also indicate some of the representative color coordinates for the lustrous bronze, copper-gold, burgundy, bluish-black, and shiny black coatings of the present invention. However, the range of chromaticity coordinates presented in Table 2 is only a subset of the range of colors which can be made by the present invention. For the present invention, the range of chromaticity coordinate values for x are from approximately 0.25 to 0.50, and for y are from approximately 0.25 to 0.45, and values for Y are from approximately 5 to 50.

The previous discussion, Examples and the results presented in Table 1 demonstrate that highly durable and abrasion-resistant composite diamond-like carbon coatings with controllable color can be applied to a variety of metal substrates by the ion-assisted plasma deposition process of the present invention. For example, coated golf club heads such as drivers, putters and irons, which have high abrasion resistance and a shiny black color, or lustrous colors such as bronze, copper-gold, burgundy, bluish-black and black can be produced. Because of the high coating deposition rates which can be attained, the invention provides an economical manufacturing process.

From the foregoing description, one of ordinary skill in the art can easily ascertain that the present invention provides an improved method for producing highly durable, lustrous protective coatings on a variety of metal substrates. Highly important technical



advantages of the ion-assisted plasma deposited composite diamond-like carbon coatings present invention includes attractive cosmetic appearance with a variety of colors, tailorable shiny, high-luster or low-luster finish, outstanding adhesion and durability, outstanding resistance to scratches, abrasion and corrosion, and ease and flexibility of mass production.

Without departing from the spirit and scope of this invention, one of ordinary skill in the art can make various changes and modifications to the invention to adapt it to various usages and conditions. As such, these changes and modifications are properly, equitably, and intended to be, within the full range of equivalents of the following claims.

## WHAT IS CLAIMED IS:

1. An abrasion-resistant coated product comprising an electrically conductive substrate coated on at least one surface with a composite diamond-like carbon decorative coating, said decorative coating comprising at least a first layer of Si-doped diamond-like carbon containing the elements C, H and Si, using ion-assisted plasma deposition and using carbon-containing and silicon-containing precursor gases selected from the group consisting of hydrocarbon, silane, organosilane, organosilazane and organo-oxysilicon compounds, and mixtures thereof, the resulting abrasion-resistant decorative coating having the properties of a Nanoindentation hardness in the range of about 5 to about 35 GPa and a thickness in the range of about 1 to about 25 micrometers.
2. The product of Claim 1 wherein said color exhibits reflected light chromaticity coordinate values (x,y) values for x of about 0.25 to about 0.50, and for y of about 0.25 to about 0.45, as measured with CIE 1931 source C standard illuminant and CIE 1931 2-degree standard observer.
3. The product of Claim 2 wherein the color of said decorative coating is selected from the group consisting of light yellow, bronze, copper-gold, burgundy, bluish-black, and black.
4. The product of Claim 1 wherein said decorative coating also contains the elements selected from the group of N and O.
5. The product of Claim 1 wherein said decorative coating comprises at least a second layer of diamond-like carbon containing the elements C and H deposited using ion-assisted plasma deposition using a hydrocarbon gas.
6. The product of Claim 5 wherein said second layer also contains the element N.
7. The product of Claim 1 wherein said substrate is the shaft of a golf club.
8. The product of Claim 1 wherein said substrate the head of a golf club.
9. The product of Claim 8 wherein said golf club is a putter.
10. The product of Claim 8 wherein said golf club is a driver.
11. The product of Claim 8 wherein said golf club is a wedge.

12. The product of Claim 8 wherein said golf club is an iron.

13. An abrasion-resistant coated product comprising the shaft of a golf club coated on at least a portion of the outer surface with a composite diamond-like carbon decorative coating, said decorative coating comprising at least one layer of Si-doped diamond-like carbon containing the elements C, H and Si, using ion-assisted plasma deposition and having the properties of Nanoindentation hardness in the range of about 5 to about 35 GPa and thickness in the range of about 1 to about 25 micrometers.

14. The product of Claim 13 wherein the color of said decorative coating is black.

15. An abrasion-resistant coated product comprising the head of a golf club coated on at least a portion of the outer surface with a composite diamond-like carbon decorative coating, said decorative coating comprising at least one layer of Si-doped diamond-like carbon containing the elements C, H and Si, using ion-assisted plasma deposition and having the properties of Nanoindentation hardness in the range of about 5 to about 35 GPa, modulus in the range of approximately 50 GPa to approximately 300 GPa, and thickness in the range of about 1 to about 25 micrometers.

16. The product of Claim 15 wherein the color of said decorative coating is black.

17. The product of Claim 15 wherein said golf club is a putter.

18. The product of Claim 15 wherein said golf club is a driver.

19. The product of Claim 15 wherein said golf club is a wedge.

20. The product of Claim 15 wherein said golf club is an iron.

21. The product of Claim 1 wherein said substrate is selected from the group consisting of brass hardware, brass fixtures, jewelry, medical instruments, dental instruments, writing instruments, musical instruments, eyeglass frames, cigar lighters, cigarette lighters, automobile ornaments, cycling equipment, fishing equipment and hunting equipment.

22. The product of Claim 1 wherein said hydrocarbon compound is selected from the group consisting of methane, butane, acetylene, cyclohexane and mixtures thereof.

23. The product of Claim 1 wherein said silane compound is selected from the group consisting of silane, disilane, diethylsilane, tetramethylsilane and mixtures

thereof.

24. The product of Claim 1 wherein said organosilazane compound is selected from the group consisting of hexamethyldisilazane, tetramethyldisilazane and mixtures thereof.

5        25. The product of Claim 1 wherein said organo-oxysilicon compound is selected from the group consisting of hexamethyldisiloxane, tetramethyldisiloxane, ethoxytrimethylsilane, octamethycyclotetrasiloxane, and mixtures thereof.

26. The product of Claim 5 wherein said hydrocarbon is selected from the group consisting of methane, butane, acetylene, cyclohexane and mixtures thereof.

10       27. The product of Claim 1 wherein said precursor gases consist of a mixture of tetramethylsilane and cyclohexane.

28. The product of Claim 1 wherein said precursor gases consist of a mixture of hexamethyldisilazane and cyclohexane.

15       29. A method for producing an abrasion resistant decorative coating on at least one surface of an electrically conductive substrate by:

ion-assisted plasma depositing from carbon-containing and silicon-containing precursor gases a composite diamond-like carbon decorative coating, said decorative coating comprising at least one layer of Si-doped diamond-like carbon containing the elements C, H and Si;

20       said precursor gases selected from the group consisting of hydrocarbon, silane, organosilane, organosilazane and organo-oxysilicon compounds, and mixtures thereof; using a substrate bias voltage in the range of about -100 Volts to about -1000 Volts; recovering a product coated with said abrasion resistant decorative coating having the properties of a Nanoindentation hardness in the range of about 5 to about 35 GPa and a thickness in the range of about 1 to about 25 micrometers.

25       30. The product of Claim 29 wherein said colors exhibit reflected light chromaticity coordinate values (x, y) values for x of about 0.25 to about 0.50, and for y of about 0.25 to about 0.45, as measured with CIE 1931 source C standard illuminant and CIE 1931 2-degree standard observer.

31. The product of Claim 29 wherein said colors also exhibit reflected light chromaticity values (Y) of about 5 to about 50.

32. The method of Claim 29 wherein the color of said decorative coating is selected from the group consisting of light yellow, bronze, copper-gold, burgundy, bluish-black, and black.

33. The method of Claim 29 in wherein the ion-assisted plasma is a capacitively-coupled RF plasma.

34. The method of Claim 29 wherein the ion-assisted plasma is a DC plasma.

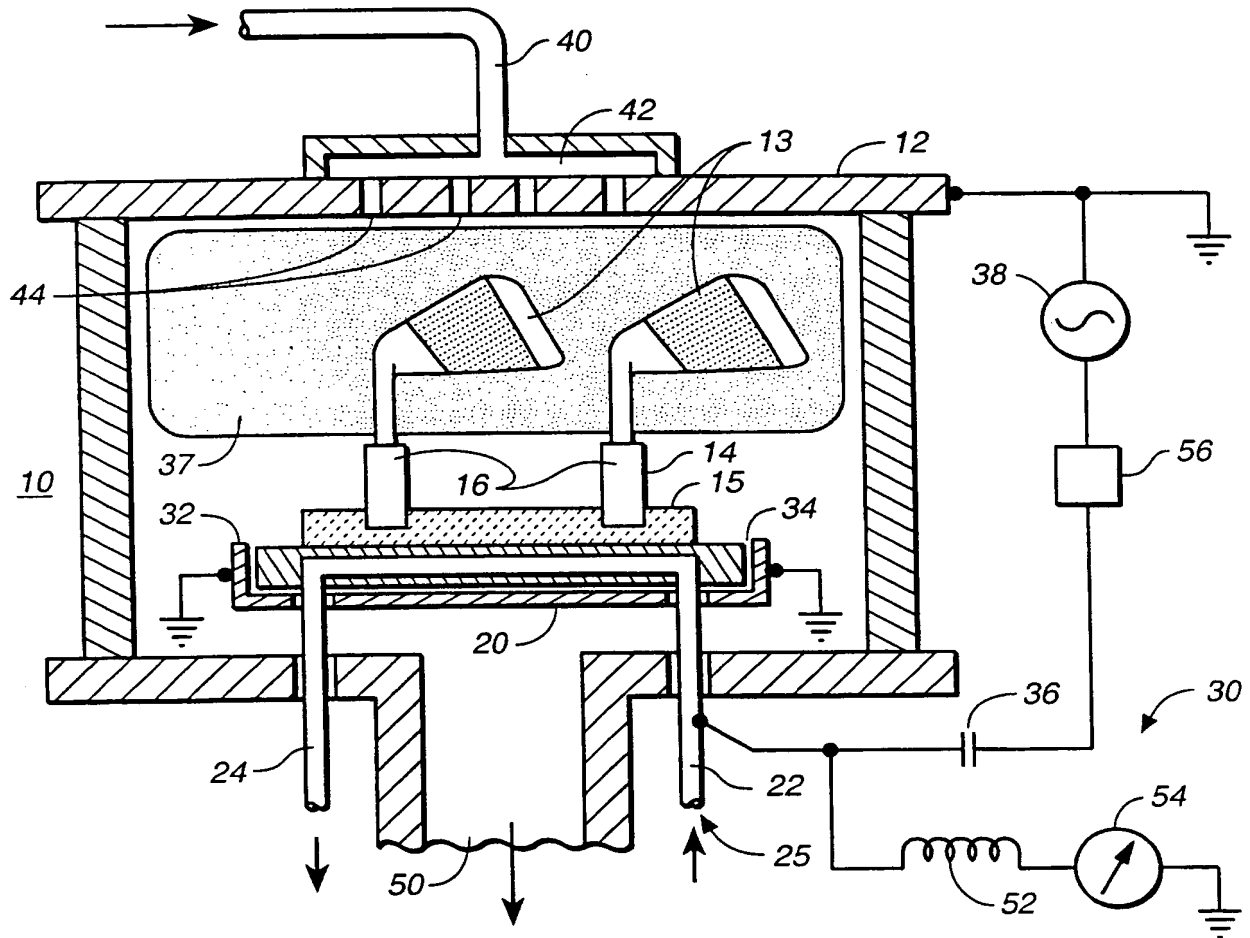
35. The method of Claim 29 wherein an ion beam source is used to generate the ion-assisted plasma.

36. A method for producing an abrasion resistant decorative coating on at least one surface of an electrically conductive substrate by ion-assisted sputter depositing a composite diamond-like carbon decorative coating, said decorative coating comprising at least one layer of Si-doped diamond-like carbon containing the elements C, H and Si, said coating having the properties of a Nanoindentation hardness in the range of about 5 to about 35 GPa and a thickness in the range of about 1 to about 25 micrometers.

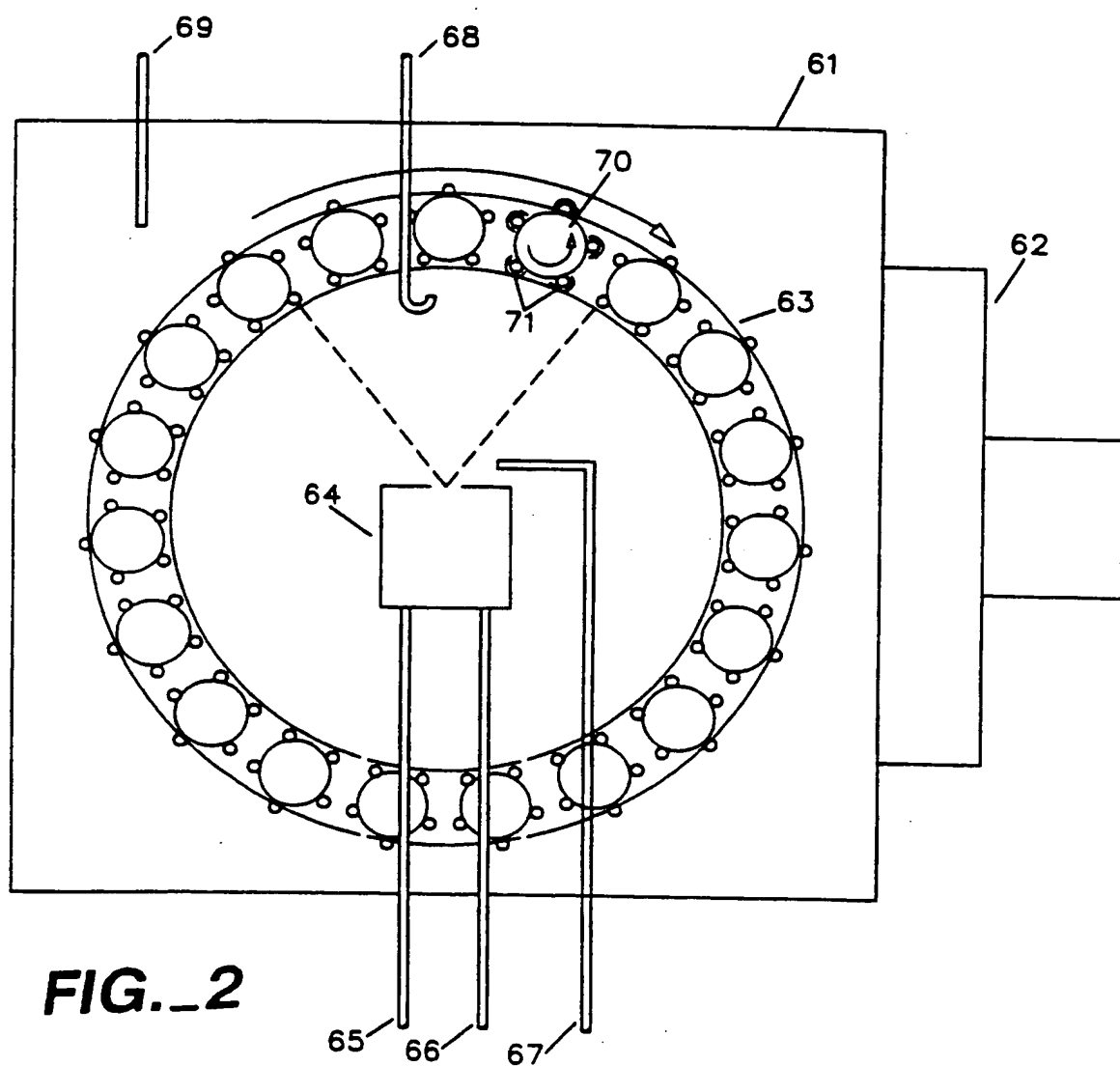
37. The product of Claim 36 wherein said colors exhibit reflected light chromaticity coordinate values (x, y) values for x of about 0.25 to about 0.50, and for y of about 0.25 to about 0.45, as measured with CIE 1931 source C standard illuminant and CIE 1931 2-degree standard observer.

38. The product of Claim 22 wherein said colors also exhibit reflected light chromaticity values (Y) of about 5 to about 50.

39. The method of Claim 22 wherein the color of said decorative coating is selected from the group consisting of light yellow, bronze, copper-gold, burgundy, bluish-black, and black.



**FIG. 1**

**FIG.\_2**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/04199

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A 63B 53/04, 53/12

US CL : 473/316,349

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 473/316,349

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 5,728,465 A (DORFMAN et al) 17 March 1998, abstract, col. 1, lines 29-33, col. 2, lines 15-24, 44-46, 55-65, col. 3, lines 32-37, 65-67, col. 4, lines 30-37, col. 5, lines 9-11, 48-51, col. 7, lines 24-54, col. 8, lines 8-12, 30-46, col. 9, lines 1-5, 23-61, col. 10, lines 15-20, col. 16, lines 1-4.	13,15,36 ----- 1-12, 14, 16-23, 25-26,29-35,37-39.
Y	EP 0 776 989 A1 (HARTMANN et al) 06 April 1997, (equivalent-US 5,900,289 A, abstract, col. 1, lines 13-16, col. 2, lines 1-4, 57-67, col. 3, lines 55-58, col. 4, lines 16-19, 27-29, 52-57, 65-67, col. 5, lines 23-32, 52-67, col. 6, lines 16-19, 61-67, col. 7, lines 31-35, col. 8, lines 13-20)	1-12, 14, 16, 21-23, 25-26, 29-35, 37-39



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

07 JUNE 1999

Date of mailing of the international search report

18 JUN 1999

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/04199

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US Re. 33,735 A (RUMBLE et al) 05 November 1991, col. 3, lines 62-65.	7
Y	US 4,754,971 A (KOBAYASHI) 21 July 1986, figure 4, col. 1, lines 33-38.	8, 11-12, 19-20
Y	US 5,344,140 A (ANDERSON) 06 September 1994, col. 3, lines 114-19).	8, 10, 18.
Y	US 1,622,864 A (FINDAY) 29 March 1927, page 1, lines 41-45.	9, 17

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/04199

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS:DLC, DLM, diamond-like carbon, silicon, hydrocarbons, hydrogen, silane, hardness, thickness, nanoindentation, chromaticity, chromatic, cyclohexane, organosilazane, hexamethyldisilazane.